Estimation of kenitic and isotherm parameters for sorption of Cd^{2+} unto hydroxyapatite from aqueous solutions

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Abstract— Hydroxyapatite is an effective adsorbent for removing cadmium from aqueous solution. In this study, Hydroxyapatite was used to investigate the removal of Cd^{2+} in the concentration range of 25-144 $mg.l^{-1}$ and the effect of contact time was studied. The application of kinetics and isotherm models of cadmium sorption on Hydroxyapatite was thoroughly examined. The adsorption kinetics well fitted using a pseudo second-order kinetic model indicating the adsorption process to be chemisorption. The intraparticle diffusion model described that the intraparticle diffusion was not the only rate-limiting step. The adsorption isotherm data could be well described by the Langmuir as well as Temkin and freundlich equations. The maximum adsorption capacity of Hydroxyapatite for Cd^{2+} was found to be 113.64mg g^{-1} at 297 K. Thermodynamic parameters (i.e., change in the free energy (ΔG^o), the variation of the energy of adsorption (ΔQ), were also evaluated. The overall adsorption process was exothermic and spontaneous in nature. These results suggest that Hydroxyapatite could be employed as an efficient adsorbent for the removal of cadmium from contaminated water sources.

Index Terms— Cadmium, Adsorption, Hydroxyapatite, Isotherms, Kinetic models.

◆

1 INTRODUCTION

The presence of metals in aquatic environments is generally from industrial units, of the mining activity and some agricultural uses. Some metals, called trace elements, are essential (Fe, Cu, Zn, ...), but in very small quantities; they allow the operation of certain metabolisms as well in plants, animals and humans [1]. In large quantities, they can certainly cause toxic side effects [2-3]. Other heavy metals such as Pb, Hg, Cr and Cd are, however, highly toxic even in trace amounts. Cadmium is one of the most toxic heavy metals due to the absence of a homeostatic control of this metal in the human body [4]. Its toxicity is known since the 50s. Very toxic in all its forms (metal, vapor, salts, organic compounds), Cadmium is one of the few elements that have no known function in the human body or in animals. In humans, it causes including kidney problems and are increased tension [5]. The toxic effects of cadmium are not only for humans but also for plants and animals [6]. In recent years, the adsorption is the most widely used technique for the treatment of waters rich in cadmium and other metal species, by its high efficacy, the ease in implementation and also the availability of low-cost adsorbents. Also other treatment techniques of polluted water are expensive and produce sludge that requires resources for their treatment [7-12]. Recently, many works have focused on the use of apatites, particularly hydroxyapatite as an adsorbent for the removal of metal ions in solution [13-15], fluoride [16], protein and phenol separation [17]. Hydroxyapatite has received considerable attention because of its industrial interests, technology and biotechnology. It is used as a catalyst in deferent reactions such as dehydration of alcohols, the oxidation of methane.

Our work is more particularly, the determination of the adsorption performance of cadmium onto hydroxyapatite. This study was conducted by the application of kinetic models and adsorption isotherms.

2 EXPERIMENTAL METHODS

2.1 Used materials

The apatite support used as extractant matrix was developed by the Laboratory of Electrochemistry and Surface Treatment of the Faculty of Sciences of El Jadida, Morocco. The Hydroxyapatite calcium phosphate has the chemical formula:

$$Ca_{10}(PO_4)_6(OH)_2$$

2.2 Preparation of sorbent

We introduce a mass of the Hydroxyapatite equivalent to 0.04 g in a filter bag (bag made filter paper). Thus the prodect is protected and levies can be made directly in the metallic solution without problem drive from the grains in the samples assayed.

The adsorption capacity was calculated using the following relation:

$$q_e = (C_o - C_e).\ V/m$$

With: q_e: adsorbed amount of cadmium on the hydroxyapatite at equilibrium ($mg.g^{-1}$).

C_o: Initial concentration of cadmium in solution ($mg.l^{-1}$).

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C_e: Concentration of cadmium in solution at equilibrium (mg.L^{-1}).

V: Volume of solution (l).

2.3 Preparation of aqueous solution

Cadmium solutions are prepared by dissolving cadmium nitrate salt $Cd(NO_3)_2$ in distilled water. The pH of the solution is adjusted with concentrated nitric acid.

3 RESULTS AND DISCUSSION

3.1 Effect of initial Cd^{2+} concentration

The effect of initial concentration of cadmium on the extent of removal in terms of amount of the cadmium adsorbed on the Hydroxyapatite adsorbent has been studied with a fixed mass of adsorbent (0.04 g) and constant agitation time at (25 °C), by varying the initial concentration of cadmium between 25 – 144.3 mg/L. The effect of initial concentration on the sorption of cadmium on hydroxyapatite is presented in Figure 1.

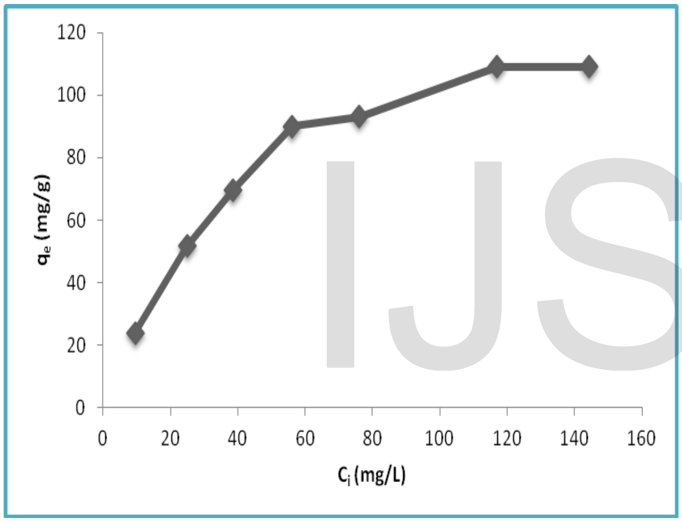

Figure 1. Effect initial concentration of Cd^{2+} in in the supernatant solution.

It is noted that the amount of cadmium adsorbed on the hydroxyapatite adsorbent, increases exponentially with the increase in the initial concentration of the cadmium.

3.2 Effect of contact time

A quantity equal to 0.04 g of hydroxyapatite was contacted with a solution of cadmium nitrate at a concentration of 9.55 mg/l; the pH of the solution was adjusted to 5. The mixture was agitated. We realized the kinetics of complexation of cadmium in solution, taking samples at regular intervals in order to know the time at which there is saturation of the Hydroxyapatite of metal.

The effect of contact time on the sorption of cadmium on hydroxyapatite is presented in Fig.2.

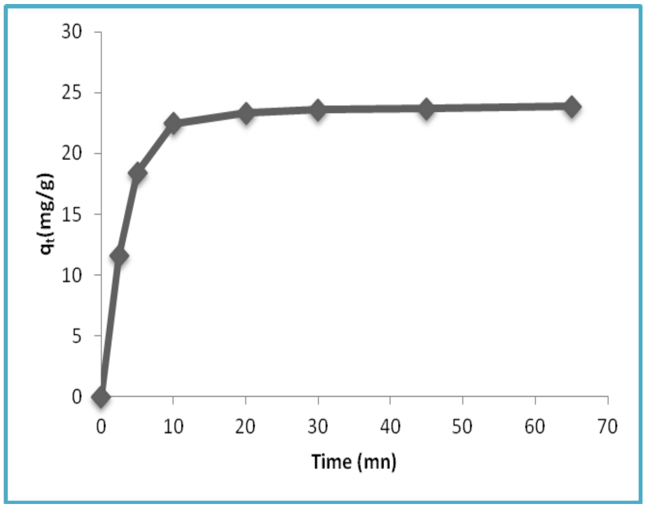

Figure 2. Effect of contact time [Cd^{2+}]=9.55 mg/l, V=100 ml, $m_{adsorbent}$=0.04 g).

These experimental data show that cadmium extraction equilibrium by Hydroxyapatite is reached about 30 minutes stirring system. The curves obtained show that almost all the cadmium was recovered under our experimental conditions.

3.3 Kinetic study of adsorption process

The kinetic models are used to model the much system kinetics and determining certain parameters such as the kinetic rate constant and the adsorbed amount at equilibrium as a function of operating conditions. Those constants are significant for designing an effective process. In this study we used the first, pseudo second order [18, 19], Intraparticular diffusion and Bangham models [20]. The equations of different kinetic models are shown in table 1.

TABLE 1

THE EQUATION OF KINETIC MODELS STUDIED

Model	Linear expression
Pseudo first-ordre [21]	$log\ (q_e - q_t) = log\ (q_e) - \frac{k_1}{2.303} t$
Pseudo second-ordre [22]	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$
Intraparticular diffusion [23]	$q_t = k_i . t^{1/2} + X_i$
Bangham [24]	$log\ log\left(\frac{C_0}{C_0 - q_t .m}\right) = \log\left(\frac{K_B}{2.303 .V}\right) + \alpha\ logt$

Where k_1 is the rate constant, q_e is the cadmium equilibrium concentration (mg/g); qt (mg/g) is the amount of adsorbed cadmium at any time t(min).

k_2 is the equilibrium rate constant (g/mg.min) of pseudo-second-order chemical sorption; q_e is the amount of adsorption sorbed at equilibrium (mg/g); q_t is the amount of adsorbate sorbed at t (min).

3.3.1 Application of kinetic models

Applying kinetic models to the experimental results is shown in Figures (3-6).

The parameters of Pseudo first-order, Pseudo second-order, Intraparticular and Bangham kinetic models are summarized in the Table 3.

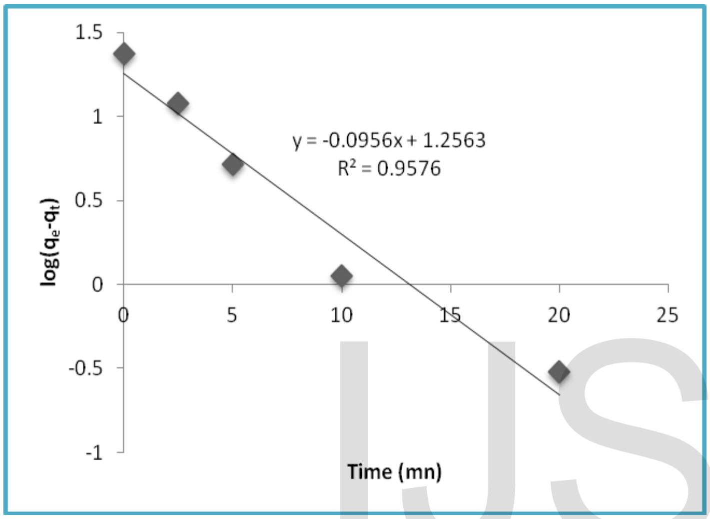

Figure 3. Pseudo-first order kinetic model.

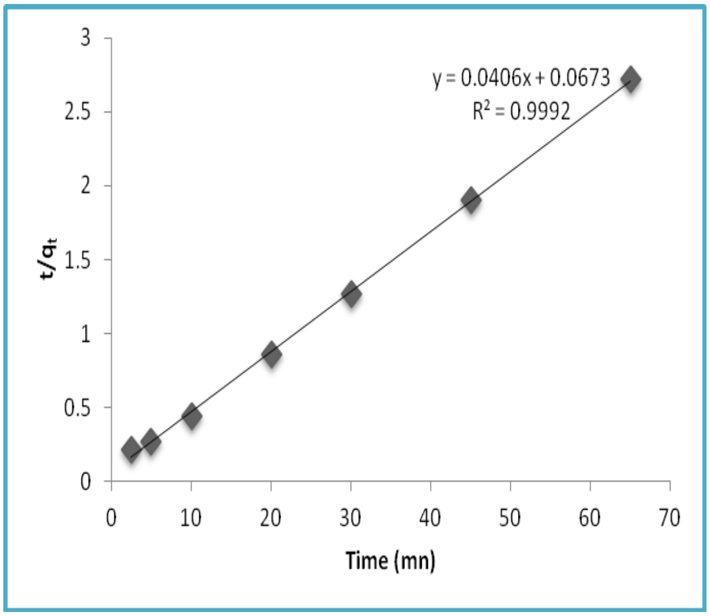

Figure 4. Pseudo-second order kinetic model.

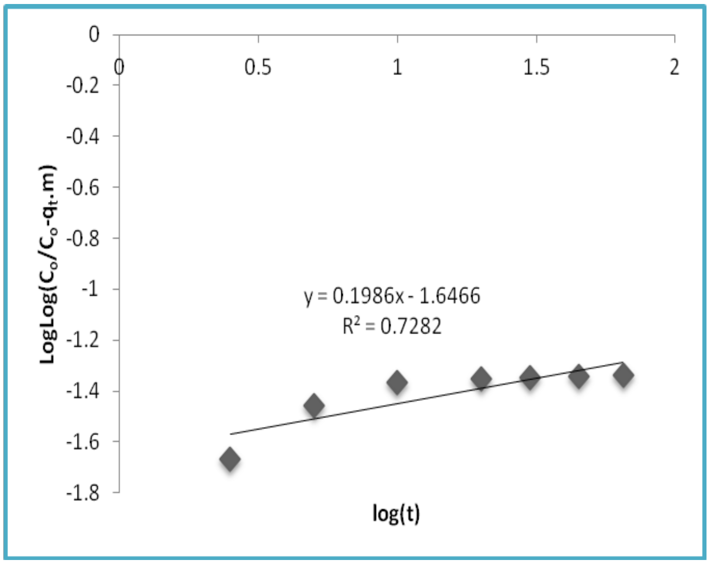

Figure 5. Bangham kinetic model.

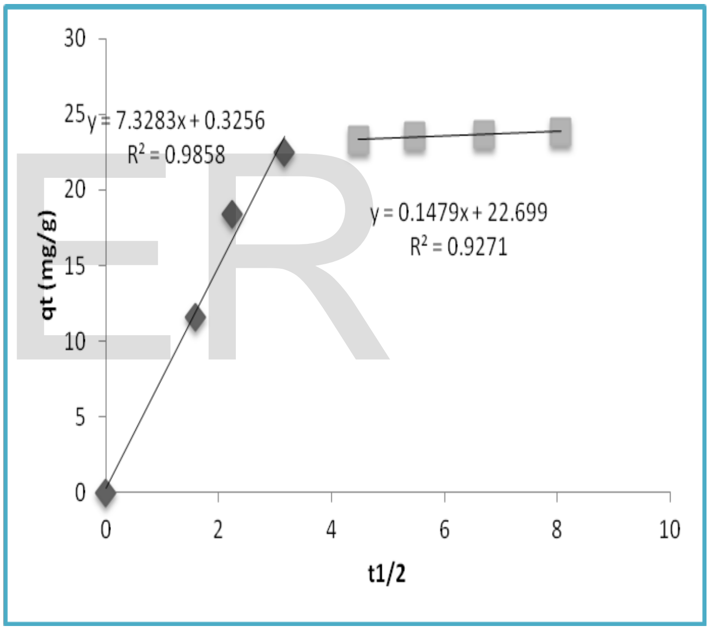

Figure 6. Inraparticular diffusion kinetic model.

TABLE 2

KINETIC MODELS PARAMETERS OF CADMIUM ADSORPTION ONTO HY-

DROXYAPATITE.

<table>
<tr><th colspan="5">Pseudo-first order</th></tr>
<tr><th>$q_{e,exp}$ (mg.g^{-1})</th><th>$q_{e,theo}$ (mg.g^{-1})</th><th>RD%</th><th>k_1 (min^{-1})</th><th>R^2</th></tr>
<tr><td>23.875</td><td>18.04</td><td>32.34</td><td>0.22</td><td>0.9576</td></tr>
<tr><th colspan="5">Pseudo-second order</th></tr>
<tr><th>$q_{e,exp}$ (mg.g^{-1})</th><th>$q_{e,theo}$ (mg.g^{-1})</th><th>Relative difference (%)</th><th>K_2</th><th>R^2</th></tr>
<tr><td>23.875</td><td>24.63</td><td>3.06</td><td>0.0245</td><td>0.9992</td></tr>
<tr><th colspan="5">Intraparticular diffusion</th></tr>
<tr><th>Temps (min)</th><th>K_i</th><th>X_i</th><th colspan="2">R^2</th></tr>
<tr><td>t<10</td><td>7.3283</td><td>0.3256</td><td colspan="2">0.9858</td></tr>
<tr><td>t>10</td><td>0.1479</td><td>22.699</td><td colspan="2">0.9271</td></tr>
<tr><th colspan="5">Bangham</th></tr>
<tr><th>α</th><th colspan="2">K_B</th><th colspan="2">R^2</th></tr>
<tr><td>0.1986</td><td colspan="2">0.005</td><td colspan="2">0.7282</td></tr>
</table>

3.3.2 Comparison of the applicability of different kinetic models

Among the four kinetic models, the pseudo-second order equation generates the best fit to the experimental data of the present investigated adsorption system. The correlation coefficient obtained is greater than 0.999 and this indicates that the pseudo- second order equation is potentially a generalized kinetic model for the adsorption study. Indeed, the relative difference between the experimental value of the quantity of cadmium adsorbed by hydroxyapatite and theoretical is very low (DR=3%). which shows that the adsorption mechanism is type chemisorption.

The plot obtained by the intraparticle model does not seem to pass through the origin indicating that the adsorption is controlled by external diffusion.

The correlation coefficient of Bangham model is less than 0.75, which shows that the adsorption of cadmium is not limited by diffusion into the pores.

3.3.3 Comparison of results with literature

In previous studies, Z. Aksu [25] studied the equilibrium and kinetic modelling of cadmium (II) biosorption by C. vulgaris. The results showed that cadmium (II) uptake process followed the second-order rate expression. T. Mathialagan and All [26] studied the Adsorption of cadmium from aqueous solutions by perlite, they found that the pseudo-second-order model best described the kinetics of the reaction. The same result is found by V. K. Gupta and all [27], by studying equilibrium and kinetic modelling of cadmium (II) biosorption by nonliving algal biomass Oedogonium sp. from aqueous phase.

3.4 Equilibrium Isotherms

Equilibrium isotherm equations are used to describe experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent. The symbols and coefficients used in the equations are defined in the Nomenclature section.

TABLE 3

THE EQUATION OF EQUILIBRIUM MODELS STUDIED

Model	Linear expression
Freundlich [28]	$\log q_e = \log K_F + \frac{1}{n} \log C_e$
Langmuir [29]	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$
Temkin [30]	$q_e = B \ln A + B \ln C_e$

Where C_e is the equilibrium concentration of cadmium in solution and q_e is the amount of cadmium in Hydroxyapatite surface, q_m is the monolayer adsorption capacity, and K_L is the constant of the Langmuir isotherm.

k is multilayer adsorption capacity and n is adsorption intensity. A and B, are the adsorption constant of Temkin where:

$$B = \frac{RT}{\Delta Q}$$

ΔQ is the variation of the energy of adsorption.

Figure (7) shows the adsorption isotherm of cadmium unto Hydroxyapatite in aqueous solution.

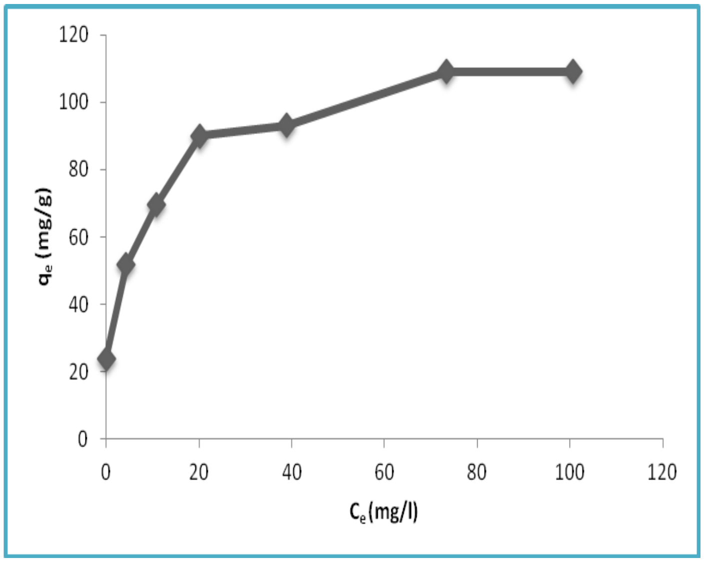

Figure 7. Adsorption isotherme of cadmium unto hydroxyapatite in 25°C.

At temperature studied, the free energy of adsorption $\Delta G°_{ads}$ can be calculated by the following equation:

$$\Delta G°_{ads} = - RT(\ln K_L+4.02)$$

$\Delta G°_{ads}$, R, K_L and T represent the free energy of adsorption, the ideal gas constant, the absolute temperature and the Langmuir constant, respectively.

The essential feature of the Langmuir isotherm can be expressed by means of the dimensionless constant separation factor [19] which is calculated using:

$$R_L = 1/(1+K_L.C_o)$$

Where K_L is the Langmuir constant and C_o is the initial concentration.

The application of Langmuir, Freundlich and Temkin isotherm models are shown in Figurs (8-10) and the evolution of R_L for adsorption of cadmium on Hydroxyapatite form aqueous solution is shows in figue 11. The parameters are summarized in table 4.

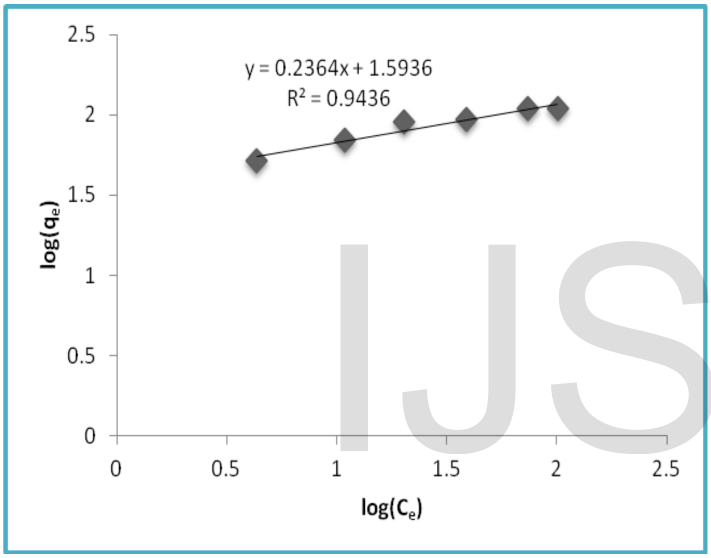

Figure 8. Freundlich isotherm model.

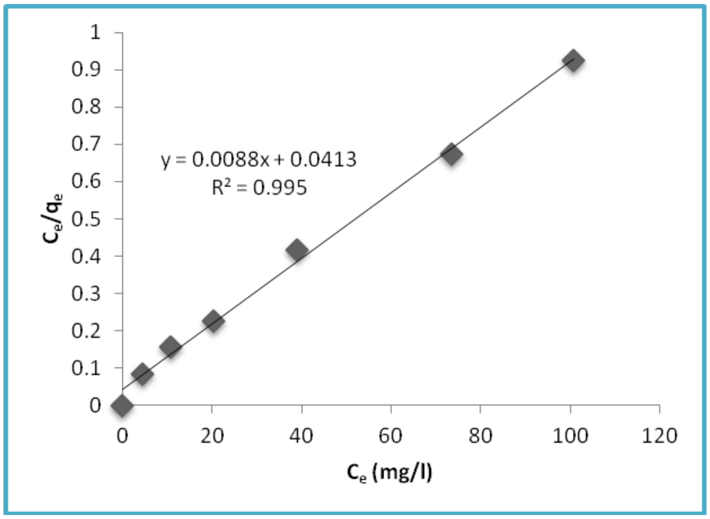

Figure 9. Langmuir isotherm model.

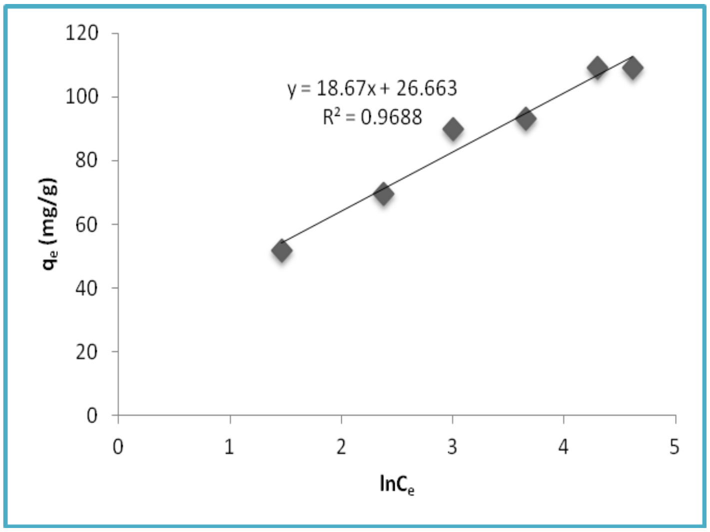

Figure 10. Temkin isotherm model.

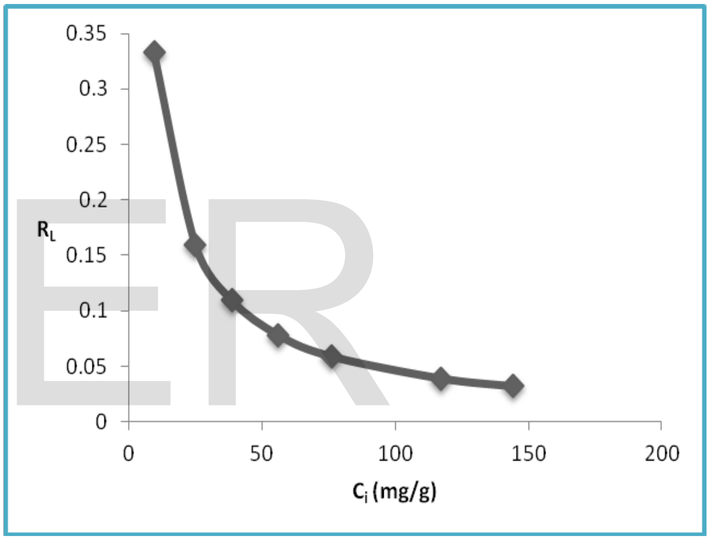

Figure 11. Evolution of separation factor.

TABLE 4

LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERM MODEL PARAMETERS.

<table>
<tr><th colspan="6">Freundlich</th></tr>
<tr><th colspan="2">1/n</th><th colspan="3">K_F</th><th>R^2</th></tr>
<tr><td colspan="2">0.24</td><td colspan="3">39.23</td><td>0.94</td></tr>
<tr><th colspan="6">Langmuir</th></tr>
<tr><th>$q_{m, theo}$ (mg.g^{-1})</th><th>Relative difference (%)</th><th>K_L</th><th>ΔG^0_{ads}</th><th>R_L</th><th>R^2</th></tr>
<tr><td>113.64</td><td>4.08</td><td>0.21</td><td>-6.1</td><td>$0.032<R_L<0.33$</td><td>0.995</td></tr>
<tr><th colspan="6">Temkin</th></tr>
<tr><th colspan="2">A (L.mg^{-1})</th><th>ΔQ</th><th colspan="2">B_1</th><th>R^2</th></tr>
<tr><td colspan="2">26.79</td><td>132.7</td><td colspan="2">18.67</td><td>0.92</td></tr>
</table>

From the Freundlich plot the values for 1/n can be calculated. The values for 1/n and R^2 for Hydroxyapatite are 0.24 and 0.94 respectively. The 1/n value suggests that the adsorptionCu (II) acting on the surface of the Hydroxyapatite was favorable.

The correlation coefficient R^2 of Langmuir is the closest of the unit compared to other models $R^2 = 0.995$, which shows that the experimental results are well represented by the Langmuir isotherm model with a favorable adsorption. Indeed, the relative difference value RD between the experimental and the therethorial value of q_m is less than 4.1% and the estimated values of R_L are less than 0.5, The increased presence of Cd^{2+} ions in the supernatant solution favors adsorption on Hydroxyapatite.

This model suggests that all adsorption sites are equivalent and the ability of cadmium to adsorb at a given site is independent of the occupation of neighboring sites and the adsorption is the adsorption is monolayer.

The negative value of ΔG°_{ads} shows that the reaction of adsorption of cadmium on Hydroxyapatite is spontaneous.

Temkin isotherm model shows that the reaction of adsorption is exothermic $\Delta Q = (-\Delta H)$ with with a higher correlation coefficient than 0.96, the solution balances its temperature by yielding heat in the environment.

Similar phenomenon has observed in the literature for the adsorption of cadmium, copper and silver on various adsorbents [31-35].

4 CONCLUSION

This study showed that the cadmium extraction equilibrium by hydroxyapatite is reached about 30 minutes stirring system. The curves obtained show that almost all the cadmium was recovered under our experimental conditions. The amount of cadmium adsorbed on the hydroxyapatite adsorbent, increases exponentially with the increase in the initial concentration of the cadmium.

The Experimental results follow the Pseudo-second order kinetic model ho suggest that the adsorption of Cd^{2+} ion from aqueous solution by Hydroxyapatite is made by chemisorptions.

The Langmuir isotherm model has the highest linear regression wich shows that:

- The adsorption is monolayer and all adsorption sites are equivalent and the ability of cadmium to adsorb at a given site is independent of the occupation of neighboring sites.
- Spontaneous which was shown by the negative value of the standard free energy ΔG°_{ads} .

Applying Temkin isotherm model to the experimental result shows that the adsorption reaction is exothermic; the solution balances its temperature by yielding heat in the environment.

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